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RAPID COMMUNICATION

The influence of disorder on the space charge field formation in photorefractive polymers

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Abstract. Recent holographic time-of-flight experiments in photorefractive polymers have shown the space charge field to depart from its expected behaviour. We show that this discrepancy arises due to the influence of disorder on the charge transport process.

Photorefractivity, which is a property of certain electrooptic photoconductors, allows reversible storage of volume holograms to be achieved using very weak laser beams. Naturally, photorefractive materials are attractive candidates for utilization in optical data storage and processing schemes, a fact that stimulated extensive studies of inorganic crystals like $LiNbO_3$, $BaTiO_3$ etc [1]. Since the first observation of the photorefractive effect in a carefully prepared polymer in 1991 [2], a great deal of research interest is being focused on the understanding and improvement of the properties of these novel photonic materials [3, 4].

When light is incident on a photorefractive material, photogenerated charges migrate from the illuminated to the dark areas, where they get trapped. The resulting charge redistribution creates an internal electric field, the space charge field, which changes the refractive index via electrooptic effects. In inorganic photorefractive crystals, the process of the space charge field formation is understood in terms of photogeneration and trapping of charges at impurity levels within the energy gap and transport in the conduction or valence band [5]. The dependence of the space charge field on material parameters is established, even in crystals with multiple impurity levels and simultaneous electron and hole conduction [6].

Although the picture of the space charge field formation in photorefractive polymers is similar to that in inorganic crystals, the individual processes of charge generation, transport and trapping in polymers are very different [7]. Charge transport, for example, takes place via hopping in a manifold of localized states, that are given in the polymer structure with the addition of specific donor-like (for hole transport) or acceptor-like (for electron transport) molecules or monomers. Understanding the extent to which these differences affect the space charge field formation, is very important for the optimisation of their photorefractive response.

Transient holographic experiments provide an indispensable tool for studies along these lines [8]: an interference pattern from two pico- or nano-second laser pulses creates a sinusoidal distribution of mobile carriers, which drifts under the influence of an external electric field. As charge separation advances, the space charge field E_{SC} builds up, which can be probed by measuring the diffraction efficiency $\eta(t)$ [9]:

$$\eta(t) \propto \left(r_{eff} E_{SC}(t)\right)^2 \tag{1}$$

where r_{eff} is the effective electrooptic coefficient.

In a holographic time-of-flight (HTOF) experiment, one monitors the diffraction efficiency as the mobile charges drift along several grating spacings. As a result of repeated coincidence and anticoincidence with the immobile distribution of countercharges, the space charge field goes through several maxima and minima, which is reflected in an oscillatory behaviour of the diffraction efficiency. This behaviour has been verified in inorganic photorefractive crystals [9].

Recently, HTOF experiments were carried out in photorefractive polymers and a different behaviour of the space charge field was observed [10, 11]. In figure 1, a typical HTOF trace from the composite poly(N-vinylcarbazole):2,4,7-trinitro-9-fluorenone:4-(hexyloxy)nitrobenzene (PVK:TNF:HONB) is shown. Instead of displaying an oscillation, the diffraction efficiency reaches a maximum and then decays to a plateau value. This behaviour, which was found to be independent of the

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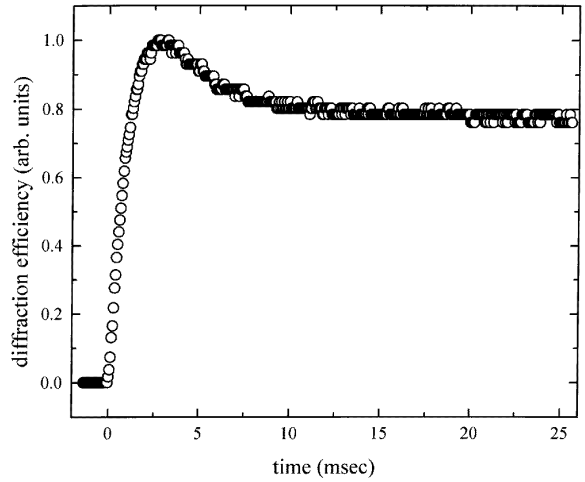

Figure 1. A typical HTOF signal from the composite poly(N-vinylcarbazole):2,4,7-trinitro-9-fluorenone:4-(hexyloxy)nitrobenzene (PVK:TNF:HONB) (see [11] for experimental details).

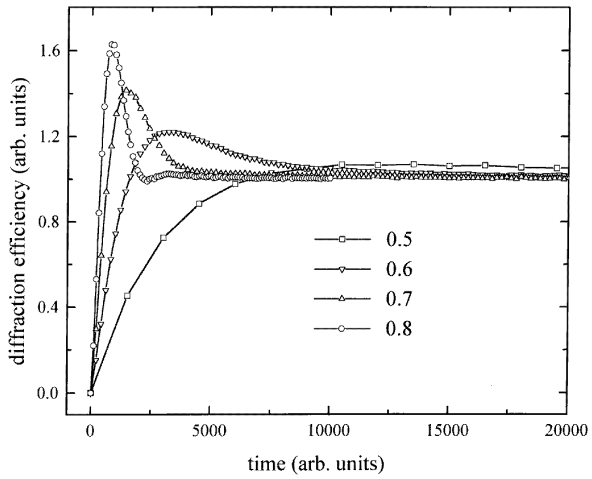

Figure 2. Simulated HTOF traces for various values of the disorder parameter a and $\Lambda_G = 200$. The lines are guides to the eye.

grating spacing, was suggested to arise as a result of the distinct, non-Gaussian character of charge transport in disordered media like polymers [11].

Charge transport can be viewed as an accumulated sequence of charge transfer steps from one localized site to another. According to this picture, each carrier independently undergoes a random walk, biased into one direction by an applied electric field. The entire character of a propagating packet of carriers depends on a key feature, the hopping time probability distribution $\psi(t)$. In an ordered single crystal, where the hopping rate W is constant, $\psi(t)$ is given by [12]:

$$\psi(t) \propto exp[-Wt] \tag{2}$$

and the charge packet exhibits normal Gaussian transport. In disordered systems, however, there is a wide distribution of hopping rates, leading to a large range of hopping times that extend well into the experimental time scale. In this case, probability distributions of the form

$$\psi(t) \propto t^{-(1+a)} \qquad 0 < a < 1 \tag{3}$$

proposed by Scher and Montroll [13], have been very successful in interpreting the shape of the current transient in conventional time-of-flight (TOF) experiments in polymers and amorphous semiconductors. Such probability distributions imply an extremely large hopping time dispersion which can arise from relatively small variations between the distance and the mutual orientation of the hopping sites (the carbazole units in PVK:TNF:HONB). The mean position of a spatially biased, time-evolving packet of charge carriers that undergoes a random walk with a probability distribution like in equation (3) varies as [13]

$$l(t) \propto t^{a} \tag{4}$$

and it is a sublinear function of time, giving rise to the peculiar character of charge transport in disordered media. Such a sublinear temporal dependence is a direct result of the presence of disorder: as time progresses, more and more charge carriers will encounter one site that corresponds to a long hopping time and get temporarily immobilized, a situation which is analogous to deep trapping. The parameter a measures the degree of disorder [14]: when $a \rightarrow 1$, the mean position $l(t)$ increases linearly with time, as in the case of Gaussian transport. Smaller a's are associated with a higher degree of disorder.

In order to examine the predictions of the Scher and Montroll theory for the case of the HTOF experiment, a computer simulation was carried out. A charge was allowed to move on a regular one-dimensional lattice, with a probability distribution like that in equation (3), biased by an external electric field [13]. The bias factor was selected to be equal to one, meaning that only steps towards one direction where allowed. Recombination and space charge field effects due to the immobile distribution of countercharges were not taken into account, which is justified by the fact that when changing the contrast of the interference pattern in the experiment, no change was observable in the HTOF shape [11]. One million charges were allowed to undergo a random walk and subsequently a distribution, $G(y, t)$, of carrier density versus distance y from the origin at a given time t was calculated. The convolution $H(x, t)$ of this distribution with a sinus function gives the spatial density of the mobile carriers at time t in a HTOF experiment

$$H(x, t) = \int \mathrm{d}y\, G(y, t) \sin\left[2\pi(x - y)/\Lambda_G\right] \tag{5}$$

where Λ_G is the grating spacing.

The diffraction efficiency was calculated from the amplitude $A^*(t)$ and the phase shift $\varphi^*(t)$ of $H(x, t)$

$$\eta(t) \propto 1 + (A^*(t))^2 - 2A^*(t)\, \cos\left[2\pi\varphi^*(t)\right] \tag{6}$$

In figure 2, simulated HTOF traces for various values of a are shown. For $a = 0.5$ the diffraction efficiency merely

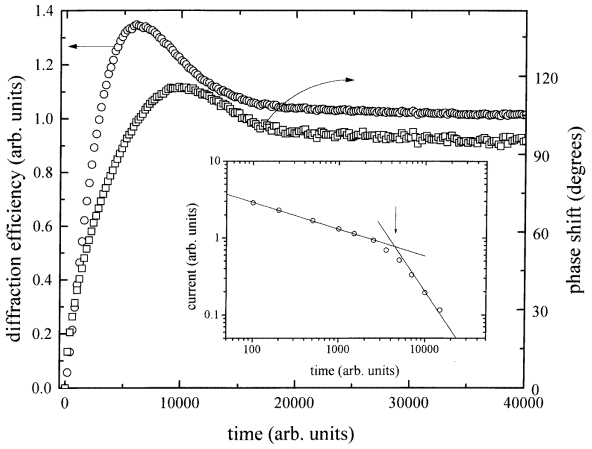

Figure 3. A simulated HTOF trace and the phase shift of $H(x, t)$ with respect to the immobile distribution of the countercharges for a = 0.65 and Λ_G = 400. Inset: simulated TOF current transient for a = 0.65 and sample thickness equal to 200. The lines indicate the theoretically predicted behaviour with slopes −0.35 (short times) and −1.65 (long times). The arrow indicates the transit time.

reaches saturation, but as a increases, the tendency towards oscillatory behaviour is apparent. The simulation resembles the experimental data of figure 2 for a's in the range of 0.6–0.7, which corresponds to the value of 0.66, measured in PVK with a conventional time-of-flight experiment [15]. No further oscillation in this range of a's was observed, even if Λ_G (which, in figure 2, is equal to 200 times the distance between two hopping sites) was changed several times.

The absence of oscillation can be understood by examining the phase of $H(x, t)$ (figure 3), which stays in the neighbourhood of 90°, instead of increasing continuously, as in the case of Gaussian transport. This comes as a result of the propagation characteristics of a charge packet, undergoing a random walk with a long-tailed probability distribution like that in equation (3): The position of the maximum of the distribution does not coincide with the position of the mean, but stays almost invariable with time [13].

An important parameter that characterizes charge transport and is accessible from a HTOF experiment is the drift mobility μ, defined as

$$\mu = L_{dr}/\left(E_0 t_{tr}\right) \tag{7}$$

where L_{dr} is length over which the charge carriers drift in time t_{tr} (transit time) under the influence of an applied field E_0. In the case of inorganic crystals the drift mobility is calculated from a HTOF transient, with the assumption that the maximum diffraction efficiency corresponds to the situation where the mobile carriers have drifted to a position of anticoincidence (i.e. 180°) with the immobile distribution of countercharges (that is, $L_{dr} = \Lambda_G/2$ and t_{tr} is the time that corresponds to that maximum) [9]. This assumption, which is intuitive for Gaussian transport, is no longer correct for the case of dispersive transport: The maximum of the diffraction efficiency in figure 3 occurs when the mobile carriers have shifted slightly more than 90° with respect to the immobile distribution of the countercharges. Thus, the calculation of the exact value of the transit time is not straightforward.

As the timescale in the simulation is in arbitrary units and cannot be related to material parameters, a simulation of a TOF current transient was carried in order to provide an indication of the transit time. Carriers were allowed to move on a regular one dimensional lattice with 200 sites (equal to half the grating spacing in figure 3), using a probability distribution like that in equation (3) with $a = 0.65$ [13]. In the inset of figure 3, the simulated TOF current transient is shown. The lines with slopes equal to $-1 + a$ and $-1 - a$ are the predictions of the Scher and Montroll theory for short and long times respectively, and their crossing point defines the transit time [12]. The crossing point occurs approximately for $t = 4300$, while the maximum of the simulated HTOF trace in figure 3 is at $t = 6000$. Thus, the mobility in a HTOF experiment is underestimated by approximately a factor of 0.7.

The Scher and Montroll theory was chosen here for the discussion of the HTOF traces due to its simplicity. It has, however, several shortcomings. For example, it fails to predict the correct electric-field dependence of the hole drift mobility [11], while it anticipates a dependence of μ on the drift length, in disagreement with the experiment [11, 16]. These discrepancies arise from the fact that in systems where not only fluctuations in the distance and the mutual orientation of the hopping sites but also in their energy are important, the hopping time probability distributions are generally more complex than simple algebraic ones [19]. Still, equation (3) can be viewed as a good approximation when limited time intervals are concerned, leading to a correct description of the shape of the HTOF traces.

In conclusion, by using a computer simulation based on the theory of Scher and Montroll, the dynamics of the space charge field formation process in a photorefractive polymer were understood. In view of this work, it would be very interesting to study photorefractive polymers where the charge transport functionality is provided by molecules like 4-(N,N-diethylamino)benzaldehyde diphenylhydrazone (DEH) or N-N′-biphenyl-N-N′bis(3-methylphenyl)-[1,1′-biphenyl]-4, 4′-diamine (TPD). Charge transport in solid solutions of these molecules is believed to be non-dispersive [20] and in this case the HTOF signal should show an oscillatory behaviour.

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